

## HISTORICAL PROFILE OF CHLORINATED PARAFFINS AND POLYCHLORINATED BIPHENYLS IN A SEDIMENT CORE FROM LAKE THUN (SWITZERLAND)

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### Abstract

A dated sediment core from Lake Thun covering the last 120 years was analysed to get an overview of the historical trend of the chlorinated paraffin (CP) and polychlorinated biphenyl (PCB) deposition. The application of CPs and PCBs are similar, e.g. as plasticisers, flame retardants and cutting oils. Total CP concentrations obtained by GC-EI-MS/MS show a steep increase in the 1980s and a more or less stable level of 50 ng/g from then. The analysis of higher chlorinated SCCPs by GC-ECNI-LRMS revealed an increase of this class in recent years, which indicates its enhanced use. Furthermore, PCBs were analysed in the sediment samples by GC-EI-HRMS. The PCB concentrations peaked around 1969 (17.7 ng/g) and decreased to 1.3 ng/g in the surface layer corresponding to 2004. CP concentrations exceeded those of PCB by ca. a factor of three suggesting a much more pronounced use.

### Introduction

Chlorinated paraffins (CPs) are produced since the 1930s and their global annual production is estimated to be about 300'000 t.<sup>1</sup> Due to varying carbon chain length they are subdivided into short chain CPs (SCCPs, C<sub>10-13</sub>), medium chain CPs (MCCPs, C<sub>14-17</sub>) and long chain CPs (LCCPs, C<sub>>17</sub>).<sup>1</sup> They are mainly utilised as additives in metal working fluids, as flame retardants and as plasticisers.<sup>2</sup> CPs with high chlorine content (~70%) are used as flame retardants.<sup>3</sup> Due to their persistence CPs are now ubiquitous in the environment and they have a high potential for bioaccumulation. Furthermore, SCCPs are toxic to aquatic organisms and carcinogenic in rats and mice. They are now under discussion for inclusion into the Stockholm Convention. Currently, information about environmental levels is scarce compared to other persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and toxaphenes. Actually, only a few data about CP levels in the Swiss environment are obtainable.<sup>4-6</sup>

CPs have similar properties as the well known PCBs. The latter was partly used for the same applications such as additives in cutting oils, paints, coatings, sealings, and as plasticisers. Industrial production of PCB mixtures started in the 1930s and stopped in the 1970s. In this time, about 1'300'000 t of PCBs were produced.<sup>7</sup> In Switzerland, the use of PCBs in open systems such as printing inks, sealants and cutting oils was banned in 1972.<sup>8</sup> In 2004, the Stockholm convention on POPs issued a ban of PCBs in 128 countries.

The aim of this work was to get an overview of the historical trend of CP and PCB deposition in a dated sediment core from Lake Thun for the last 120 years. Analyses of dated sediment cores are an excellent way to investigate concentration trends over decades. The CP and PCB time trends were compared with each other.

### Materials and Methods

*Chemicals.* Solvents and reference standards for CP analysis have been published in detail elsewhere and hence only the additional chemicals for the PCB analysis are described.<sup>9</sup> Toluene for dioxin and PCB analysis was obtained from Biosolve (Vallenswaard, Netherlands). The internal <sup>13</sup>C<sub>12</sub>-PCBs standard mixture with the congeners 28, 52, 101, 138, 153, 180 was purchased from Cambridge Isotope Laboratories (Andover, USA) and the recovery standard <sup>15</sup>N<sub>3</sub>-musk xylene (1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, <sup>15</sup>N<sub>3</sub>-MX) was synthesised in our laboratories.

*Glassware pre-treatment.* Extreme care was used to maintain the CP contamination at the lowest possible level. Therefore, glassware was cleaned with acetone, dichloromethane (DCM) and *n*-hexane (nHex) after a normal washing procedure (glassware washer and alkaline bath). Then, the glassware was backed out at 450 °C overnight. Before use, the glassware was rinsed again with DCM and nHex.

**Sediment core samples.** A sediment core of Lake Thun was collected on May 18th, 2005 near the mouth of the river Aare (near the village Därligen) at a depth of 60 m. Lake Thun is located in the alpine region of the Canton Bern in the centre of Switzerland and has a surface area of 47.69 km<sup>2</sup>, a mean depth of 136 m, and a volume of 6.42 km<sup>3</sup>. The core was 1.1 m in length and 56 mm in diameter and was cut into 1 cm slices, which were lyophilised, weighted, homogenised, and stored in glass jars in the dark before dating and analysis. The sediment core was dated by <sup>137</sup>Cs and <sup>210</sup>Pb analysis which gave an average sedimentation rate of 0.45 cm per year.<sup>10</sup> 15 samples of this sediment core were analysed. Every sample consisted of a 1 cm thick slice and represented approx 2.25 years of deposited material. The surface slice corresponds to the year 2004.

**Sample clean-up.** Further details of the applied clean-up procedure are given elsewhere and hence only briefly described.<sup>9</sup> 5-10 g of dried and homogenised samples were spiked with the corresponding internal standards (CP analysis: 10 ng of <sup>13</sup>C<sub>10</sub>-*trans*-chlordane; PCB analysis: 8 ng of a <sup>13</sup>C<sub>12</sub>-PCB-Mix) and then Soxhlet extracted with 200 ml of dichloromethane and *n*-hexane (DCM/nHex, 1+1, v/v) for 8 hours. Activated copper powder was added to eliminate sulphur. After solvent evaporation, sample matrix not persistent to sulphuric acid was removed by column chromatography on 20 g of silica gel impregnated with concentrated sulphuric acid (44%). PCBs and CPs were eluted with 70 ml of DCM/nHex (1+1, v/v). Further fractionation was carried out on 16 g of Florisil<sup>®</sup> (1.5% water content) eluted with 75 ml of nHex and 5 ml of DCM (first fraction) and 60 ml of DCM (second fraction). The first fraction containing PCBs was concentrated and the solvent was changed to toluene. The remaining solvent was concentrated to about 100 µl and transferred to a GC vial containing the recovery standard (9.84 ng of <sup>15</sup>N<sub>3</sub>-MX). The second fraction contained all CPs and was concentrated to 0.5 ml and the solvent was changed to cyclohexane. Finally, the extract was reduced to 100 µl and 10 ng of ε-HCH in 10 µl of cyclohexane were added as recovery standard.

**Instrumentation.**

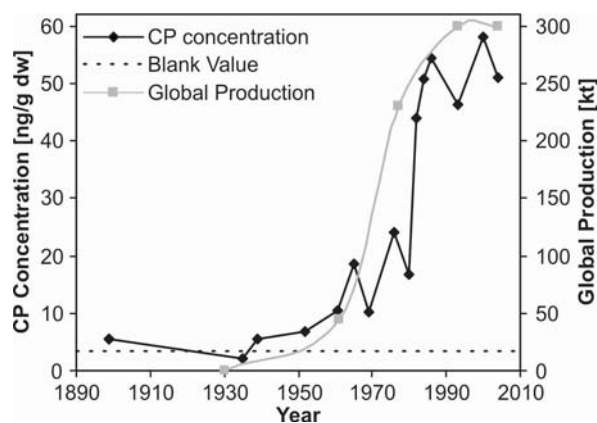
**CP analysis – GC-EI-MS/MS.** Parameters for the EI-MS/MS analysis of CPs are published in detail elsewhere and hence only changes are described.<sup>11</sup> The fragmentation masses were slightly modified for the determination of the total CP amount: *m/z* 91 → *m/z* 53 (collision energy: -10 V), *m/z* 102 → *m/z* 67 (-10 V) and *m/z* 104 → *m/z* 67 (-10 V).

**CP analysis – GC-ECNI-MS.** Parameters for the determination of homologue profiles and chlorination degrees by ECNI-MS are described elsewhere.<sup>12</sup> The CP profile evaluation was performed according to Reth et al. (2005).<sup>13</sup>

**PCB analysis – GC-EI-HRMS.** Parameters for PCB analysis are published elsewhere.<sup>14</sup>

## Results and Discussion

The historical time trend of total CP concentrations in Lake Thun is shown in Figure 1 for 1899 to 2004. Each data point represents the average age of the respective sediment samples. The concentration starts with 5 ng/g dry weight (dw) for the deeper, pre-industrial, sediment slice, and rises slowly from the 1950s to the 1970s. Then, the CP level increased from the 1980s and became more or less stable from the 1990s to present. The highest concentration of 58 ng/g dw was observed in 2000. These data are well consistent with the few data available on global production,<sup>3</sup> which is also shown in Figure 1.



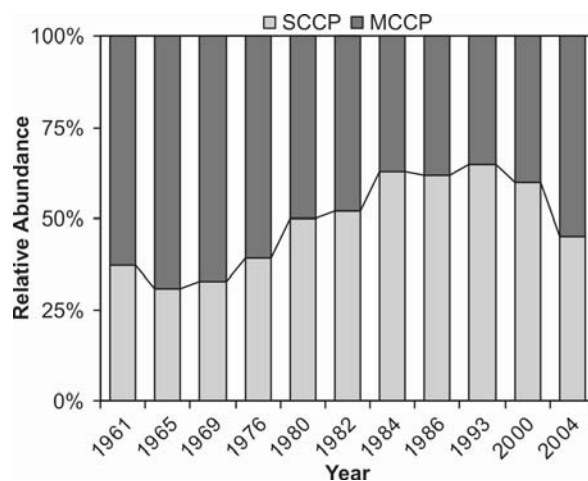
**Figure 1** Historical time trend of the total CP concentration in a sediment core from Lake Thun represented by the black continuous line. The dotted line corresponds to the blank value and the grey continuous line to the CP global production amount. The analysis was performed by GC-EI-MS/MS.

The few recent publications about surface lake sediments are from Canada (Lake Ontario<sup>15</sup>, Lake Fox and Ya Ya Lake<sup>16</sup>). The CP concentration in Lake Thun sediment was considerably lower than for Lake Ontario (49 ng/g SCCPs) and Lake Fox (257 ng/g SCCPs). The reason is a rural region around Lake Thun with low industrial activity. Only the very remote Ya Ya Lake had a lower concentration of 1.6 ng/g SCCPs. So far, only two studies have investigated the CP historical profile in a lake sediment core. Only data for SCCP were published. Therefore, a comparison with the total concentration of Lake Thun is not entirely conclusive. A sediment core from a Canadian Arctic lake (Devon Island) showed a similar increase during the past twenty years.<sup>17</sup> However, the maximum observed for 1957 could not be detected in the Lake Thun sediment. A profile from Lake Ontario had a maximum in 1970 with a concentration of about 800 ng/g dw which decreased to 400 ng/g dw in the surface slice of 1996.<sup>15</sup> The differences between these sediment cores may indicate different usage history and local sources.

The total chlorine content of selected samples is shown in Table 1. The degree of chlorination of SCCP increased from 64.2% in 1961 to 67.5% in 2004. These data suggest that more CP products of higher chlorine content were applied and released to the environment. An explanation for this observation could be a ban of alternative flame retardants such as PCBs and the use of SCCPs as substitution products. Higher chlorinated CPs are less volatile and atmospheric long-range transport is less likely.<sup>1</sup> Therefore, the data indicate the presence of local sources of CP release to the environment.

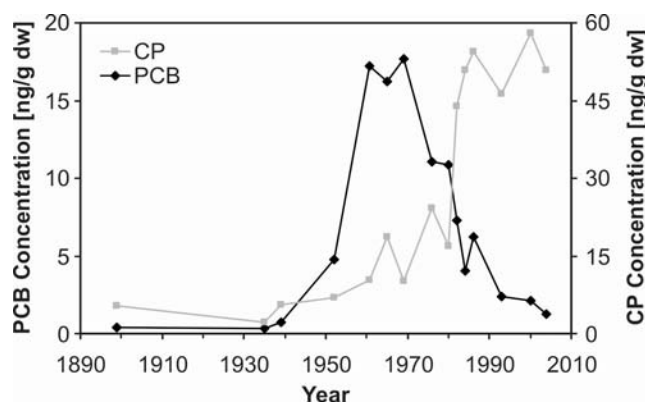
**Table 1** Total degree of CP chlorination obtained by GC-ECNI-LRMS of selected sediment core samples from Lake Thun.

Year	Chlorine content SCCPs [%]	Chlorine content MCCPs [%]
1961	64.2	53.5
1965	63.7	53.3
1969	63.7	53.3
1976	63.9	54.1
1980	65.1	54.2
1982	66.4	54.9
1984	67.4	54.1
1986	69.5	54.7
1993	68.0	56.0
2000	66.6	56.6
2004	67.5	56.1



**Figure 2** SCCP and MCCP composition of selected sediment samples from Lake Thun obtained by GC-ECNI-LRMS.

In Figure 2 SCCP and MCCP concentration of selected analysed sediment samples are compared. It is apparent that the SCCP/MCCP ratio has increased from 1965 to 2000. In 2004 a slight decrease was observed.



**Figure 3** Historical time trend of the PCB sum concentration in a sediment core from Lake Thun represented by the black continuous line. The grey continuous line corresponds to the total CP concentration. The analysis was performed by GC-EI-HRMS and GC-EI-MS/MS, respectively.

CP concentrations were compared with those of the six most commonly analysed PCB congeners 28, 52, 101, 138, 153 and 180. Figure 3 shows the historical time profile of the PCB sum and the total CP concentration. The PCB concentration at Lake Thun started to increase in 1952 and had its maximum with 17.7 ng/g in 1968. From then on, the concentration decreases to 1.3 ng/g in the surface slice from 2004. The steep decline after 1968 could reflect the use restriction of PCBs starting in the 1970s. In Switzerland, the usage of PCBs in open systems was banned in 1972. At that time CP production started to rise partly due to use as PCB substitute as well as plasticiser and flame retardant. The peak concentration of 58.0 ng/g for CPs is about a factor of three higher than for PCBs (17.7 ng/g). This correlates well with the higher global production of CPs.

*Conclusion.* The analysis of the sediment core of Lake Thun has shown that there has been a considerable deposition of CPs in the past 30 years. The concentration time profile is in good agreement with the available global production data. The ECNI analysis demonstrated that the chlorination degree of SCCP has strongly increased during the past 40 years. This suggests that technical SCCP mixtures with higher degree of chlorination usually applied as flame retardant have been increasingly employed. Comparison of PCB and CP concentrations showed that the CP concentration increased during the decline of the PCBs. This may suggest that CP products were used as substitutes for PCBs after their ban in Switzerland.

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